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PB-277 013

Characterization and Generation of Metal Aerosols

Industrial Environmental Res Lab, Research Triangle Park, N.C.

Feb 78

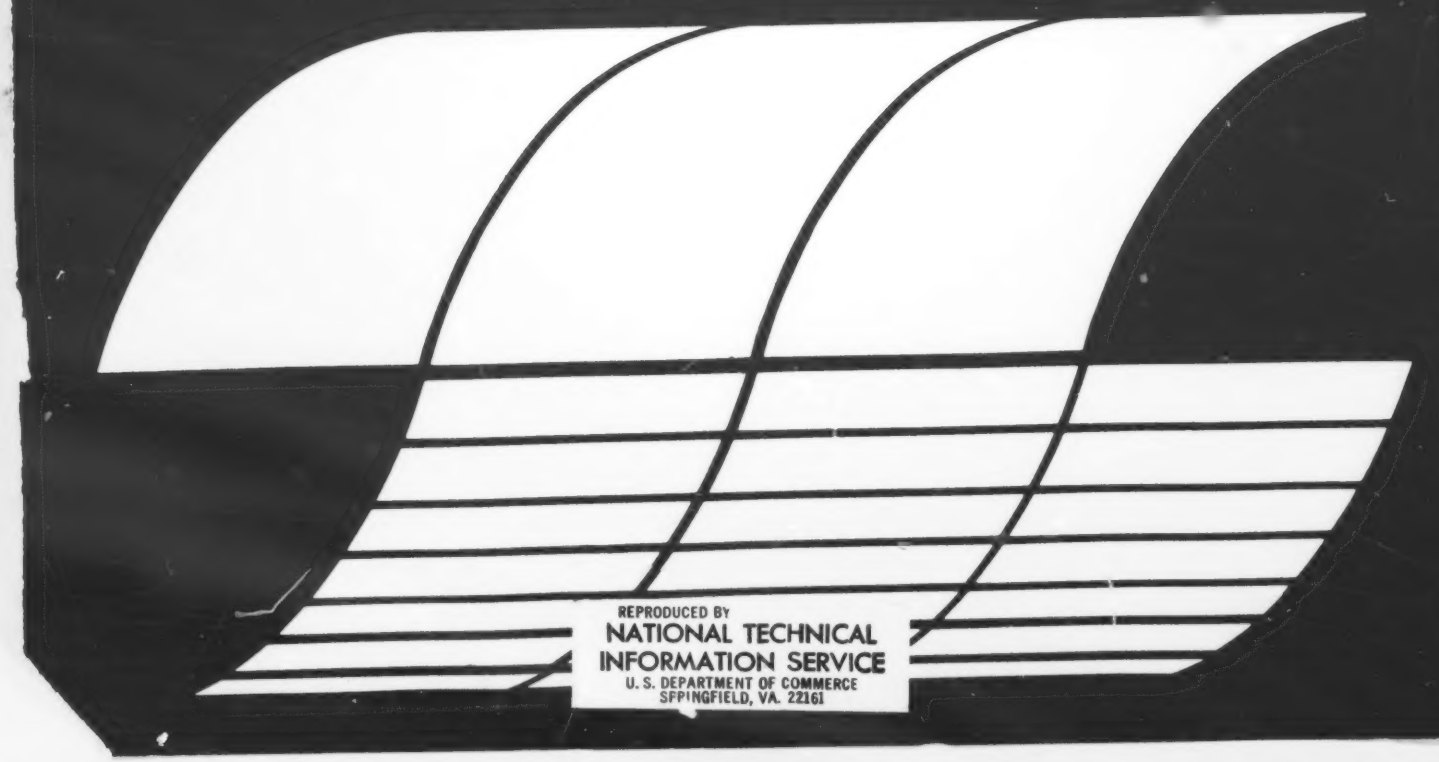
PB 277 013

EPA U.S. Environmental Protection Agency
Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

EPA-600/7-78-013
February 1978

CHARACTERIZATION AND GENERATION OF METAL AEROSOLS

Interagency
Energy-Environment
Research and Development
Program Report



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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/7-78-013	2.	3. RECIPIENT'S ACCESSION NO. PB277013
4. TITLE AND SUBTITLE Characterization and Generation of Metal Aerosols		5. REPORT DATE February 1978 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Neil Zimmerman, Dennis C. Drehmel, and James H. Abbott		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Industrial Environmental Research Laboratory Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO. EHE623 11. CONTRACT/GRANT NO. NA (Inhouse)
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 6/76-6/77 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer/author is D.C. Drehmel, Mail Drop 61, 919/541-2925.

16. ABSTRACT The report reviews techniques of metal aerosol generation for the purpose of establishing the state-of-the-art of the technology and guiding future researchers. Exposure to metal or metallic compound submicron aerosols is widespread in both industrial and general environments. Research in areas of health effects, sampling instrumentation, and air pollution control technology requires a reliable source of test aerosol. The report presents many mechanisms for generating metal aerosols, and discusses their applications, advantages, and disadvantages. Generation methods can be on a continuous or batch basis, with high or low concentrations and generation rates, and with monodisperse or polydisperse size distributions. The method chosen and the resulting aerosol depend on the requirements of the specific research being conducted. Metal aerosols generated by exploding wires, electric arcs, heating to evaporation, combustion, and dispersion are presented, with particular attention paid to particle size characteristics.

17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Exploding Wires	Air Pollution Control	13B	19A,14B
Aerosols	Electric Arcs	Stationary Sources	07D	20C
Metallurgy	Evaporation	Particulates	11F	
Aerosol Generators	Combustion	Metal Aerosols	15B	21B
Properties	Dispersions	Characterization	14B	
Testing	Size Determination			

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	54
	20. SECURITY CLASS (This page) Unclassified	22. PRICE A04, A01

EPA Form 2220-1 (9-73)

EPA-600/7-78-013
February 1978

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by

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Program Element No. EHE623

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

Abstract

The techniques of metal aerosol generation are reviewed in this report to establish the state-of-the-art of the technology and to guide future researchers. Exposure to metal or metallic compound submicron aerosols is widespread in both the industrial and general environments. Research in areas of health effects, sampling instrumentation, and air pollution control technology requires a reliable source of test aerosol. Many mechanisms for the generation of metal aerosols are presented and their applications, advantages, and disadvantages discussed. Generation methods can be on a continuous or a batch basis, with high or low concentrations and generation rates, and with monodisperse or polydisperse size distributions. The method chosen and the resulting aerosol depend on the requirements of the specific research being conducted. Metal aerosols generated by exploding wires, electric arcs, heating to evaporation, combustion, and dispersion are presented, with particular attention paid to particle size characteristics.

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Conversions

1 Å	=	10^{-4} μm
1 lb	=	454.5 g
1 in.	=	2.54 cm
1 ton	=	907.2 kg
1 m^3/min	=	35.515 ft^3/min
1 g	=	15.43 gr
1 gr/ft^3	=	2.29 g/m^3
1 ft^3/min	=	28.32 l/min

Terms and Abbreviations

d_a	=	aerodynamic diameter
d_{mmd}	=	mass median diameter
PSD	=	particle size distribution
EM	=	electron microscope
K	=	coagulation coefficient
SEM	=	scanning electron microscope
TEM	=	transmission electron microscope
n	=	concentration, particles/cm^3
σ_g	=	geometric standard deviation
CMD	=	count median diameter
MAD	=	median aerodynamic diameter

Acknowledgments

Discussions with Professor Benjamin Linsky of West Virginia University and Dr. Parker Reist of the University of North Carolina at Chapel Hill were very helpful and informative.

1 INTRODUCTION

An aerosol is basically a suspension of solid particles and liquid drops in a gaseous medium. They are throughout our environment, existing naturally and as a by-product of man's activities. Particles with diameters less than 10 mm are generally classified as aerosols. This range of particle size is important in terms of ambient air quality, health hazards, and industrial pollution control. In particular, fine submicron particles, those less than 1 μm, are of most concern with respect to visible light scattering, atmospheric dispersion, deep penetration and retention in lungs, and decrease in conventional removal mechanism efficiencies.

Aerosols can be composed of a multitude of substances depending on the materials involved in their generation. This report will be limited to a discussion of metal aerosols. The ferrous and nonferrous metallurgical refining, processing, and manufacturing industries make up one of the largest as yet uncontrolled sources of anthropogenic air pollution, second only to power plants. Because of such large amounts of metallic compound emissions, it is important to delineate the specific characteristics of these aerosols. Continued study of the physical, chemical, and biological properties of these aerosols will lead to a better understanding of their health effects as well as capabilities of controlling and reducing their emission.

A brief review of some metal particulate emission data will help to put the significance of the problem into perspective. Various sources quote wide ranges of emissions for various metallurgical facilities. Estimates of uncontrolled particulate emissions include: 8-51 lb/ton steel produced[1-4], 20-60 lb/ton Cu[4], 50-90 lb/ton Zn[4], 12-75 lb/ton Pb[4], and 81-98 lb/ton Al[4]. Comparisons with controlled emissions indicate that 99.5% control is possible for Cu, Fe, Pb, and Zn, giving emissions of approximately 0.1 - 0.5 lb/ton[4]. Controlled Al emissions are somewhat higher, in the range of 1.6 - 19.6 lb/ton[3]. These five metals comprise more than 95% of total U. S. metal consumption according to a 1976 EPA report[5]. Small amounts of Mn, TiO_2, Ni, Zr, Sn, Sb, and Mo are

also used. Even if emissions of many of the five major metallurgical industries are eventually controlled, pollution problems could still exist because of the effect of the particle size distribution on control efficiency.

Although there are references in the literature to metal aerosol particle size distributions, they vary widely, due partly to the nature of the aerosol. Fumes are a type of aerosol which result from oxidation reactions, sublimation, or condensation, mechanisms associated with the application of heat. Most metallurgical processes involve heating and melting at some stage, generating large amounts of fumes. The mechanisms that generate these fumes generally operate at the molecular level, resulting in an aerosol of largely submicron particles. These aerosols are usually polydisperse, having a wide range of diameters.

1.1 Metal Aerosols from the Iron and Steel Industry

In a review of the ferrous foundry industry, Bates and Scheel[2] found that the particle size distributions varied from 50% weight < 1 μm to 5% weight < 2 μm. The composition also varied considerably, with the iron content shifting from as much as 50% to only 5% depending on the impurities present and on the stage of the process. Other components besides iron oxides (Fe_2O_3 and Fe_3O_4) in foundry emissions are Si, Ca, Al, Mg, Zn, and Mn. Electric arc emissions, however, are mainly composed of Fe and Zn oxides and volatile matter. Bates indicates that other sources such as Holland et al. and Coulter have found electric arc emissions to be 90-95% < 0.5 μm. Another study of electric arc emissions[3] states that particle size measurements by Erickson indicate 70% weight < 5 μm, while electron photomicrographs by Allan et al. found 95% by number of the particles < 0.5 μm in diameter.

Several studies have determined the particle size distributions from iron cupolas. Two publications by Calvert[6,7] give results for gray iron and ductile iron cupolas: the mass median diameters range from 0.25 to 1.9 μm. For the Calvert data a more exact breakdown of the results is given in Table 1 which summaries data on metal aerosols from the iron and steel industry. In another study on a gray iron source,

Table 1. SUMMARY OF PARTICLE SIZE DATA FOR THE IRON AND STEEL INDUSTRY

Source	Author	Percent by Weight < 1 μm	Mass Median Diameter μm	Deviation
Foundry	Bates[2]	50	-	-
Cupola	Calvert[4]	40 - 60	0.92 - 1.15	1.7 - 2.1
Gray Iron	Calvert[5]	40 - 80	0.54 - 1.9	1.5 - 1.8
Gray Iron	Cooper[6]	80	0.5	2.4
Ductile Iron	Calvert[5]	60 - 100	0.25 - 0.84	1.5 - 2.0
Electric Arc	Bates[2]	95	-	-
Ferroalloy	McCain[7]	20	4.3	-
Ferroalloy	Drehmel[8]	15	1.7	1.9

Cooper[8] found a mass median diameter of 0.5 μm. For ferroalloy furnaces, McCain[9] determined a mass median diameter of 4.3 μm and Drehmel[10], one of 1.9 μm. It should be noted from Table 1 that for most of the iron and steel sources tested submicron sized particles ranged from 40 to 100 weight percent. The exception appears to be ferroalloy furnaces where the percentage is slightly lower (15-20 weight percent). For all sources the mass median diameter ranges from 0.25 to 4.3 μm and the geometric deviation from 1.5 to 2.4. If it is assumed that particles of 3 μm in diameter and smaller are respirable, then it may be concluded that metal aerosols from iron and steel operations are concentrated in a fairly narrow size range most of which is respirable.

1.2 Metal Aerosols from the Nonferrous Metals Industry

Estimates of aluminum emissions are 40% by weight < 1 μm and 60% by weight < 5 μm in diameter. Measurements by Hanna and Pilat[11] at a horizontal aluminum reduction cell show 30% by weight <1 μm, 16% by weight < 0.2 μm, with a mass median diameter (d_{mmd}) of 5.5 μm and a geometric standard deviation (σ_g) of 25. They felt that coagulation and diffusion to the exhaust duct wall was a factor in reducing the number of particles < 0.5 μm and shifting the particle size distribution up.

Harris and Drehmel[12] cite information by Vandegrift showing that, on the average, at least 30% of various metal particulate emissions will be less than 10 μm in diameter. Furthermore, Harris gives the PSD of the emissions from various nonferrous industrial process units. For a lead sintering machine the d_{mmd} was 0.89 μm and the σ_g was 4.4. For a zinc sintering machine, the d_{mmd} was nearly the same (0.82 μm) and the distribution more nearly monodispersed (indicated by a σ_g of 2.1). At the same plant the zinc roaster had very fine particulate emissions as indicated by 90% less than 1 μm and a d_{mmd} of 0.42 μm. The size distribution was similar with a σ_g of 2.3. For a copper converter fewer small particles were found and the d_{mmd} was the highest of the four units tested (1.05 μm). The particle size distribution was also the narrowest with σ_g = 1.7. A summary of data on metal aerosols from the nonferrous industry is given in Table 2. Note that all these nonferrous sources

Table 2. SUMMARY OF PARTICLE SIZE DATA FOR THE NONFERROUS METALS INDUSTRY

Source	Percent by Weight < 1 μm	Mass Median Diameter μm	Deviation
Al Reduction Cell	30	5.5	25
Zn Sintering Machine	60	0.82	2.1
PB Sintering Machine	55	0.89	4.4
Cu Converter	45	1.05	1.7
Zn Roaster	90	0.42	2.3

have at least 30% of their emissions in the submicron range; the percentage may be as high as 90%. The d_{mmd} range from 0.42 to 5.5 μm. Recalling that the d_{mmd} for iron and steel sources ranged from 0.25 to 4.3 μm, one may conclude that the majority of metal aerosols generated by industrial processes are between 0.25 and 5.5 μm in diameter.

1.3 Metal Aerosols Characterized from Occupational Studies

Studies have been conducted to measure the work environment of metal workers and welders to determine their exposure potential. Kolderup[13] studied the fumes from a ferrosilicon open submerged-arc furnace; he found basically a log-normal size distribution of agglomerates ranging from 0.02 to 1 μm, consisting of spherical primary particles ranging from 0.01 to 0.3 μm. The primarily silicon dioxide particles appeared to form by homogeneous nucleation between Si and O_2. The agglomerates then grew by diffusion. Health effects hazards due to nitrogen oxides (NO_x) and trace elements such as Mn were reported by McCord et al.[14], in addition to the 90-682 mg/m^3 concentrations generated with coated welding electrodes. McCord et al. indicated that, although a large part of the sample may have been < 0.5 μm, the impinger collection system did not collect these small particles. When silica-coated iron-core electric arc welding electrodes are used, particles tend to be in the size range of 0.01 to 1 μm, according to experiments by Pfefferkorn and Desler.[15] By developing a method to remove the iron oxide from the sample, they observed hollow SiO_2 spheres, indicating that the aerosol had an iron oxide core with a SiO_2 coating.

In a recent study by Stettler et al.[16], lung biopsy specimens from two arc-welders were compared with air samples from their work environment. Most of the particulate material found in both samples was iron, with other components present indicating stainless steel. Some large spherical stainless steel particles in the range 0.5 - 3 μm were found in the lung tissues, but most of the particles were clusters 0.1 - 0.2 μm in overall size, made up of individual particles as small as 0.005 μm. Six times as many irregularly shape .uminum-containing particles on the order of 1 μm were found in Case 2 (the sicker worker) than in Case 1. Although

difficulties with the filter media precluded sizing the particles from the air samples, electron micrographs did show that clusters of particles existed, made up of 0.05 μm primary particles. The authors point out that there have been many conflicting reports in the literature as to the toxicity of iron oxide and other trace materials usually found in welding atmospheres. The observations in this study emphasize the need for further characterization of welding fumes and animal inhalation studies to quantify their biological impact.

Concentrations in the breathing zone of operators exposed to two types of welding equipment, single electrode jet-arc and powder burning arc, ranged from 20 to 35 mg/m^3 in five steel plants in eastern Pennsylvania[17]. With local exhaust ventilation, the exposures dropped below the Pennsylvania Threshold Limit Value (TLV) of 10 mg/m^3. No definite connection between iron oxide fumes and health effects could be drawn from this study.

A study to assess the hazards to industrial workers exposed to metallic fumes with a median aerodynamic diameter (MAD) < 1 μm was performed by exposing rats to iron oxide aerosol[18]. Rats were exposed to Fe_2O_3 with a MAD = 0.3 μm, σ_g = 1.8, and concentrations up to 700 mg/m^3. Although the rats' lung clearance half time was shorter than man's, the Lung Dynamics Task Group model for man gave a good approximation of the lung deposition efficiencies in the rat. The values for pulmonary deposition are: 35% for 0.3 μm, 25% for 1 μm, and 10% for 5 μm. Results also indicated that depositions in organs other than the lung are insignificant for relatively insoluble particles such as iron oxide. Casarett and Epstein[19], in another rat inhalation study, found an average deposition rate of 60% when using a tagged iron oxide aerosol with a count median diameter (CMD) of 0.068 μm (σ_g = 1.62). There was a 3 to 1 ratio between upper and lower respiratory tract deposition with 10-15% alveolar deposition.

1.4 Characteristics of Generated Metal Aerosols

A fundamental requirement for any study or project involving the examination of certain properties of aerosols is a controllable source of those aerosols. Laboratory generated aerosols can be used in many

areas of air pollution research; e.g., biological studies involving inhalation and particle deposition; sampling instrumentation development, verification, and calibration; development and evaluation of air pollution control equipment; and evaluation of industrial hygiene ventilation and safety equipment.

Many factors must be taken into consideration if a useful representative aerosol is to be produced. The concentration of the aerosol in the gas stream can vary considerably, depending on the method of generation. The concentration to be generated depends on the needs of the research: levels less 1 mg/m^3 would be useful for ambient studies; values to several hundred mg/m^3 would apply to industrial hygiene and animal inhalation studies; and concentrations of 1 g/m^3 and above would apply to process and stack emission analysis and control. Together with the concentration, the gas flow rate determines the generation rate (in units of mass per unit time), which is an indication of a generator's capability for a certain application.

The particle size distribution (PSD) is another factor which is radically affected by generation method. Different levels of dispersity may apply more or less to different investigations. For example, very controlled studies (e.g., development of a respiratory model or sampling instrument calibration) may require a relatively monodisperse aerosol, while control equipment testing and health effects research may be more realistically accomplished using a polydisperse aerosol, as would be the case in real life. Shape and density are two other factors which describe the overall state of the aerosol.

To generate liquid or solid aerosols the basic input requirement is energy. In general, the more energy per unit of material, the smaller is the particle size attained due to increased surface area. This energy input can take two basic forms to generate either dispersion-redistribution aerosols or condensation aerosols.[20] In the former, liquid aerosols are normally dispersed by nebulizers and sprays in various configurations, while solid particles can be redistributed by blowers, grinders, vibrators, or resuspension in liquids. Condensation aerosols are created by heating a material to the vapor state, by combustion, or by chemical reaction.

Many good reviews of aerosol generation are available[20-23] which discuss various techniques and mechanisms involved in this important field. This report will examine these topics as they apply specifically to metal aerosols. Although this sometimes involves overlap with techniques (such as nebulization) applicable to liquids or solids, other techniques (such as exploding wires and electric arcs) are unique to the generation of metal aerosols.

Researchers have been interested in the characteristics of metal aerosols since the early 1950's. Advances in generating and analyzing aerosols in the past 5 years have increased the desirability of using submicron diameter metal particles. The major generation techniques that will be reviewed are: exploding wires; electric arc, both low and high intensity; vaporization; combustion; and liquid resuspension systems and associated thermal treatment. Inherent in many of these methods will be factors influencing the quality and usefulness of the aerosol. Such factors include the freshness or staleness of the material, the moisture content and temperature of the aerosol-gas stream system, and the presence of combustion products and other gases.

Condensation processes will be discussed first. In general these processes (e.g., exploding wires, electric arcs, combustion, and vaporization) produce very high concentrations of very small particles, with large size distributions. The high concentration promotes rapid agglomeration by diffusion, which changes the particle size distribution.

2 EXPLODING-WIRE GENERATORS

The general principle of this method is to conduct as much stored electrical energy through a thin piece of wire in as short a time as possible. Both amount of energy and time of transfer are important parameters. If the amount of energy transferred exceeds that which would cause surface evaporation, the wire expands as a superheated vapor until it explodes. The wire thus changes state and becomes a charged plasma of metal vapor which cools and condenses into a submicron metal aerosol. The plasma consists of the metal vapor and ionized gas. Thermal coagulation and Brownian diffusion occur rapidly, creating

charged chained groups of particles. A basic series of texts containing extensive information on the exploding wire phenomenon was compiled by Chase and Moore[24] during the period 1958-1968. More recent literature reviewing characteristics of the aerosols is presented in a chronological manner.

Metal aerosols from exploded wires of 15 different materials were studied by Karioris and Fish.[25] With a current surge from a discharging 4000 joule capacitor, spherical metallic or metal oxide particles with a CMD of 0.02 μm are formed. This median diameter was observed to decrease with an increase in voltage. Although agglomerate sizing was not done, coagulation occurred quite rapidly and could be observed directly in a Tyndall beam. By diluting in the ratio of 20 to 1 and mixing for an hour, a stable aerosol of mostly isolated spherical primary particles could be attained. Duerksen et al.[26] improved upon the previous exploding-wire generator with construction of a smaller, self-contained unit. They reported obtaining reproducible spherical particles in the range of 0.01 - 0.1 μm for use in studies of particle properties when exposed to various humidity, radiation, and gaseous contaminant conditions. Other investigators[27] using the same equipment studied tagged SO_2 adsorption rate with aerosols generated from exploded Fe, Al, and Pb wires. They reported that chemisorption accounted for a monolayer coating of SO_2 on the particles but physical adsorption continued to add up to 75 times as thick a layer of SO_2.

A modification was developed by Tomaides and Whitby[28] which altered the energy triggering method. In their generator, the wire was brought into contact with a fixed electrode, completing the electrical circuit and discharging the energy. They also observed the relationship of decreasing the CMD and the σ_g as specific charge energy (energy per unit length) was increased. A typical aerosol generated by this process had a CMD = 0.03 μm and σ_g = 2.0. The aggregates formed by these primary particles, however, experienced an increase in CMD with an increase in specific charge energy. It was theorized that the smaller particles promoted greater coagulation, ultimately resulting in a larger but log-normal distributed chained aggregate aerosol.

Phalen[29] investigated the properties of an exploded silver wire aerosol with particular emphasis on an evaluation of its suitability for inhalation studies. He determined the coagulation constant to be 2 x 10^{-9} cm^3/sec, with an initial concentration of 10^9 particles/cm^3, suggesting a coagulation half-time of approximately 0.5 seconds. Accordingly, he aimed a sharp blast of air (2 liters) at the wire cloud, triggered within a few tenths of a second after the explosion to delay the coagulation. A large dilution factor then maintained a stable aerosol with a mean aerodynamic diameter (MAD) of 0.3 μm. Due to the configuration of the agglomerated aerosols with their greatly increased surface area per volume, the particles are more chemically reactive at the surface, can retain more electric charge, and can be more easily solubilized. These factors can affect aerosol interaction with biological systems and make them more hazardous than was previously expected.

Rather than simply characterizing the aerosol, Sherman[30] concentrated on the relationship between the particle size characteristics and the actual amount of energy transferred to the wire. With his circuitry and measuring instrumentation, he was able to determine the energy, in joules, as a function of time, in microseconds. Transmission electron microscope (TEM) analysis of Ag, Cd, and Zn aerosol collected on mica coated plates (positioned 8 cm from the wire) indicated that the mean particle size decreased as energy transfer increased. That is, the faster the metal expansion, or explosion, the greater the supersaturation and rate of nucleation. He observed that Cd and Zn had a narrower size distribution than the Ag aerosol. This may be explained by the fact that Ag, having a larger surface tension, would tend to have a slower nucleation rate yielding a wider size distribution of nuclei. It is interesting to note that Sherman saw no change in PSD over several minutes--the electron photomicrographs showed that almost no agglomeration took place. His major observations (when no chemical reactions occurred and pure metal aerosols formed) were: particles were spherical in shape and ranged from 0.005 to 0.1 μm in diameter; the PSD was roughly log-normal; and the mean particle size was inversely proportional to the energy transferred per unit length of wire.

Just as the energy transfer that Sherman studied is one of the most critical parameters in determining aerosol characteristics prior to the explosion, the phenomenon of agglomeration or coagulation, seen by most experimenters, is one of the most critical parameters after the explosion. Wegrzyn[31] studied the effect the bipolar charge has on the stability of the generated aerosol. Using a gold wire, exploded in an argon-filled chamber, he observed an aerosol whose primary particle mean diameter ranged from 0.01 to 0.1 μm with a typical effective diameter of 0.032 μm. The percentage of charged particles was slightly less than 50%. The charge concentration of his aerosol (approximately 100,000/cm^3) was well within the capabilities of a 2 millicurie Krypton-85 neutralizer at a flow rate of 10 l/min. Wegrzyn then compared the concentration in particles/cm^3 over a 30 minute period after the explosion with and without exposure to the neutralizer to observe the coagulation coefficient (K) with respect to time. After the aerosol was neutralized to a standard Boltzman distribution of charge, K was fairly stable within a range of 21-29 x 10^{-10} cm^3/sec; however, without neutralization, values of K were approximately a factor of 2 higher during the first 600 seconds, before dropping to the lower values. He also noticed an increase in the total mass concentration with respect to time which may indicate the increasing vapor adsorptive capability of the coagulating aerosol. His results reinforce previous findings that exploding wire aerosols are reproducible (submicron, normal, or log-normal) in primary particle size distribution and highly charged.

Radioactive tagged iron oxide aerosols from an exploding wire were analyzed by Kops et al.[32,33] with an electron microscope and a Stöber centrifugal aerosol spectrometer (which deposits the aerosol along a strip depending on the aerodynamic diameter) to study fluid drag on the chained aggregates. The electron microscope examination showed that the primary particle size distribution was approximately log-normal. From the centrifuge data of iron oxide aggregates with six different primary PSD's, they consistently observed two distinct log-normal distributed diameter ranges which depended on the concentration (n) in the chamber. For $n > 5 \times 10^3/cm^3$, the aerodynamic diameter (d_a) was proportional to $n^{1/3}$; for $n < 5 \times 10^3/cm^3$, d_a was proportional to $n^{1/6}$. Typical mean d_a values of the two regions were 0.259 and 0.925 μm. This is as expected,

since a higher concentration would tend to promote more coagulation and a wider subsequent diameter spread; whereas, a lower concentration would have a lower coagulation rate and, hence, a more monodisperse aerosol. Their results are of importance in describing the coagulation of solid particles. It has generally been assumed that smaller solid as well as liquid aerosols unite to form one large new particle, implying that the Stokes diameter of a chain aggregate equals its volume equivalent diameter. Kops et al., however, from their calculations of d_a, have shown that the Stokes diameters of chain aggregates are less than their volume equivalent diameters.

Exploding wire aerosol generators have been utilized and studied extensively for the past 30 years. Many of the phenomena are fairly well understood and, with the various refinements that have been incorporated in their use, the aerosol is quite useful and dependable in the proper application. The inherent batch operation nature of exploding wires, however, limits its usefulness when larger, more continuous quantities of aerosol are desired or required. Moreover, as shown in Table 3, the size distribution of particles generated by exploding wire techniques is very small (0.005 - 1 μm) and does not simulate industrial metal aerosols which range from 0.25 to 5.5 μm.

3 ELECTRIC ARCS

One metal aerosol generation method that is not limited to small, batch type conditions is the electric arc. The technique of striking an arc between two electrodes has been recognized since the late 19th century. Continued development led to the discovery of the high intensity arc mode by Beck in Germany in 1910. Early aerosol scientists such as Whytlaw-Gray[34] were making use of electric arcs to study the properties of metal fumes in the early 1920's. Ultramicroscopy allowed those researchers to observe particles in the 0.01 - 0.2 μm range. With the advent of electron microscopy and other advances in particle sizing and counting methodology, the study of electric arcs continued with emphasis on the characterization and use of the aerosol being generated. Research with both low and high intensity arcs has contributed to the understanding of metal aerosols.

Table 3. SUMMARY OF PARTICLE SIZE DATA FROM EXPLODING-WIRE GENERATORS

Author	Data Type	Result, μm
Karioris[25]	Count mean diameter	0.02
Duerksen[26]	Range	0.01 - 0.1
Tomaides[28]	Count mean diameter	0.03
Phalen[29]	Mass average diameter	0.3
Sherman[30]	Range	0.005 - 0.1
Wegrzyn[31]	Effective diameter	0.032
Kops[32]	Mean diameter	0.26, 0.93

3.1 Low Intensity Arcs

A low intensity arc normally consists of one or two consumable electrodes creating a gap across which an electric current can be passed in a continuous spark. A great deal of the electrical energy is transformed into thermal energy, which melts and partially vaporizes any material within the arc with a melting or boiling temperature less than the arc temperature. Typical arc-spot temperatures (actual spot on metal that arc touches) are approximately 3000°C. The exact configuration of the apparatus will determine the dispersion of the melted and vaporized metal. As the material leaves the arc zone, it rapidly cools, causing melted drops to solidify and vaporized material to condense and solidify into an aerosol. The gas in the arc zone between the anode and the cathode becomes ionized and exists as a plasma. Since the majority of the voltage drop occurs in this region, most of the energy transfer is in the form of radiant heat to the plasma rather than conductive and convective heat to the electrode which is to be melted. This condition of energy distribution is optimized with the high intensity arc which is discussed later. The aerosol generated by the low intensity arc is influenced by many input parameters such as voltage and current applied to the arc, rate of electrode consumption, and temperature in the arc zone.

Since the consumable electrode is the initial source of aerosolized metal, its physical characteristics must be understood. Amson[35] developed a model for predicting the voltage along the "stick-out" (the exposed electrode between the current pick-up point and the arc interface) in terms of arc current, wire feed rate, and exposed length. Carslaw and Jaeger[36] also present a well-developed model of temperature distribution within the electrode.

Recognizing the need for the generation capability of aerosols < 1 µm from an industrial hygiene standpoint, a group of Japanese investigators[37] generated Fe, Pb, and W aerosols with an electric arc. Rather than using a continuous DC current, they discharged 9000 volts AC intermittently (300 cycles/minute) across the electrodes. Sampling with an electrostatic precipitator sampler and analyzing with an electron microscope indicated

spherical Fe and Pb oxide particles with little agglomeration. The count mode diameter of the iron oxide was 0.02 μm; for the tungsten, it was 0.04 μm, with a general range of 0.015 - 0.15 μm. They concluded that this was a viable method of generating submicron particles, but did not attempt to explain the formation mechanisms.

Harvey et al.[38] generated many metal aerosols with a DC arc to investigate the structure and forms of the primary particles of the smokes. Electron microscope analysis confirmed earlier investigations (such as by Whytlaw-Gray et al.[34]) that all the particles formed charged chain-like aggregates. Additionally, the extent of the chain formation for Au and Ag smoke appeared to be strongly dependent on the pressure of the gaseous atmosphere. The Au and Ag aerosols (from heated wire filaments) were formed of pure metal; the other metals investigated formed oxides, except that Pb and Bi formed metal particles coated with an oxide. From electron and x-ray diffraction analysis, some typical shapes, and primary and aggregate dimensions are: ZnO--hexagonal, 4Å (1Å = 10^{-4}) primary particles, and 4000Å long rod-shaped aggregates; Fe_2O_3--cubic, 8Å primary particles, and 300Å aggregates; and Al_2O_3--cubic, 16Å primary particles, and 300-500Å agglomerates.

Although researchers had made many estimates of aerosol shape and size, Reichelt[39] was among the first to critically examine the operational parameters and their influence on the aerosol particle shape and size distribution. Experimenting with Fe, Al, and Cu electrodes in air, CO_2, argon, and N_2, he could detect no lower size limit with the capabilities of the electron microscope (size range from 100Å to 20 μm). These particles are created as some of the metal evaporates due to the high temperature at the spot where the electric arc contacts the electrode. Even if voltage and current are maintained constant, the arc cannot be considered a candidate for use as a monodisperse aerosol generator due to the nonuniform nature of the arc, which can move about quickly, changing its length and spot location. In terms of total aerosol production, current has a great influence: the weight of aerosol is proportional to the current cubed. Thinner electrodes and greater separation optimize and increase production. Analyzing particles with a Goetz aerosol

centrifuge, Reichelt found that the particles generated were not spherical and formed chains. He also noted that the current had little effect on the Stokes diameter (diameter of a sphere with the same density and settling velocity as the particle in question) particle size of the chain aggregates. Increasing the flow rate did decrease the agglomerate size, basically by diluting and dispersing the particles, reducing the coagulation rate. With electron microscope analysis it was found that current had a large effect on the size of the primary particles--an increasing current increased the size. This tends to explain the fact that the influence of current on Stokes diameter is not so pronounced, since larger particles will coagulate less. Other aerosol characteristics (e.g., the number and size of polyhedra and crystals) varied with flow rate, direction of flow (horizontal or vertical), and chemical composition. In conclusion, Reichelt felt that the arc was not an ideal aerosol generator, due to the rather uncontrolled and complex processes involved and his results of varying PSD's with consecutive samples.

Beginning with a configuration similar to Reichelt's with two electrodes inserted into an exhaust duct, Linsky et al.[40] investigated the generation of iron and zinc oxide. The initial generator consisted of one consumable wire electrode and one nonconsumable tungsten electrode. Results indicated that 75% of the agglomerated iron oxide particles were < 0.1 μm; primary particles had a mean diameter of approximately 0.02 μm. The agglomerate size data probably was altered since the measurement technique was resuspension in liquid for Coulter Counter sizing. Linsky et al. later examined a commercially available wire spray metallizer, used to coat industrial parts with a fine metal layer. The equipment consisted of two consumable wire electrodes mounted on a gun; a compressed air nozzle centered between them dispersed the melted and vaporized material. This configuration was much more controllable than the earlier one or Reichelt's equipment, and reproducible PSD's and concentrations were obtained. It was estimated that agglomeration occurred within the first 0.1 second after generation, forming highly charged chain aggregates whose mean diameter was 0.41 μm; the mean diameter of the primary particles was < 0.01 μm. The maximum aerosol generation rate of the Linsky metallizer was approximately 8 g/min which corresponded to a typical conversion efficiency of wire metal into usable aerosol of 8-15%.

Zimmerman[41] achieved similar results using identical equipment, with an approximate conversion efficiency of 4% and a highly charged, agglomerated aerosol. Approximately 80% of this aerosol had an aerodynamic diameter < 1 μm, based on a cascade impactor. More aerosol characterization work needs to be done on this system to determine if a specified set of input parameters (e.g., voltage, wire feed rate, compressed air pressure, exhaust air flow rate, and wire composition) can generate a reproducible, predictable aerosol.

3.2 High Intensity Arcs

A high intensity arc is similar in configuration to the low intensity arc. The difference lies in the current density and efficient use of the electrical energy. The high intensity arc is established at a sudden transition point when the current density exceeds a critical value for an ordinary arc. In the arc crater, the temperature can increase by more than a factor of 2 to 7000-8000°C. As previously mentioned, in the low intensity arc the largest voltage drop occurs in the plasma between the electrodes, while the remaining drop is approximately 10% across each electrode. As the arc current increases, the current density remains approximately constant as the arc crater (assuming electrode diameters larger than wires) increases on the surface of the anode until it fills the entire anode face area. Additional energy is dissipated by radiation and conduction of heat until the increased energy can't be removed fast enough. Then the anode temperature begins to rise until the boiling point is reached. Beyond this point large amounts of vapor are generated by the anode material. A superheated region develops near the anode in this tail flame which can reach values to twice the boiling point of the anode material (e.g., 4827°C for carbon; 2750°C for iron), dissociating it into elemental molecules which then recondense as they travel out of the hot zone.

The high intensity arc was proposed by Sheer and Korman[42] as a means of energy transfer in the processing of materials, such as refining of metal ores. The nonconducting portion of the electrodes can be as high as 80-85%, with the balance being carbon. They obtained silica

fumes with an average particle size of 0.03 - 0.04 μm with an 80% silica/ 20% carbon electrode. Harris et al.[43] later proposed the use of the arc for processing rhodonite for extraction of manganese from siliceous ores. No size data was given in their study.

Holmgren et al.[44] applied the high intensity arc principle specifically to submicron particle formation for industrial applications. By consuming the solid anode, a highly ionized plasma anode tail flame exists, so that there are many available condensation nuclei upon which submicron particles can form. The rapid temperature drop does not allow much particle growth leaving primary particles in the 10-1000Å size range. Increasing the dilution-cooling quench rate decreases the size. Increased quenching also decreases the initial coagulation rate by dispersion of the particles and thus limits the PSD. Agglomeration, however, cannot be avoided, and chain aggregates will form. According to the authors, the increased chemical reactivity, sintering rate, and surface energy of submicron particles make this a promising process. For the same reasons it also could be very useful in aerosol generation applications.

Although the anode temperature of a high intensity arc can reach 8000°C, the area around the cathode can achieve temperatures in the 10,000-20,000°C range.[45,46] To take advantage of this, Korman et al.[45] modified the high intensity arc configuration by using two nonconsumable electrodes and feeding the process material in powdered form in a gas stream into the arc near the cathode. They were able to obtain metal oxide particle sizes < 0.1 μm. Further refinement of the quenching process for cooling and diluting the vaporized gas is necessary to be able to better control the PSD. They achieved feed rates of 60 g/min with an estimated 40-70% vaporization of the material. This is a much higher generation rate than any other aerosol generator with the ability to form a submicron aerosol. A cyclone can be used to remove large unvaporized material allowing the submicron material to pass. It is true, however, that the feeding of material to the arc in powder form is a difficult task especially for metals.[46] Perhaps the best way to produce copious amounts of metal vapor which could condense into a submicron aerosol would be to strike an arc across a water-cooled graphite cathode and metal in a crucible, and allowing the high intensity arc mode to be reached.[46]

Researchers in Italy (Boffa and Pfender[47]) have made a similar application of the high intensity arc principle with the added variation that the quench gas transpires through the anode as the anode is ablated, or consumed. This transpiration not only provides dilution and cooling air but appears to limit coagulation as well. Their results show that they can control mean particle size between 45Å and 1 μm with σ_g < 1.2. A σ_g this low is generally considered to be a measure of practical monodispersity. The major controlling parameters are the arc current and the cooling gas flow rate. The mean particle size increases with increasing temperature, due to increased current, because the anode ablation rate increases causing a greater density of particles in the area near the anode. This increase in number of particles influences the coagulation and growth rate. The mean particle size decreases, however, with an increase in flow rate due to enhanced cooling and dispersing.

Boffa et al.[48] later altered their generation system to make it easier to use. The high intensity arc is maintained between two nonconsumable electrodes with argon gas feeding into the cathode area. The plasma jet and the argon transpire through a porous consumable matrix. The plasma ablates the matrix material while the gas quenches and dilutes the vapor. Similar PSD results were obtained with this method. No generation rate information was given for either variation of this method.

Another group of Italians, Tarroni et al.[49], developed an apparatus very similar in principle to the work of Korman et al.[45] Tarroni's group utilized a Collison atomizer (with dialyzed Fe_2O_3 suspended in argon) and a dust feeder (with iron particles) to feed the material into the plasma arc near the cathode. CMD's of 0.005 and 0.004 μm, respectively, each with σ_g = 1.3, were obtained.

A review by Fannick and Corn[50] indicates the extent of industrial hygiene hazards of plasma torches and arcs. Concentrations of various fumes generated at plasma torch facilities were presented. Many exposures of Fe_2O_3 exceed the Threshhold Limit Value (TLV) of 10 mg/m^3, ranging from 11.9 to 35.1 mg/m^3. From another source, they reported total fumes (consisting of 10% chromium) ranging from 24.5 to 31.3 mg/m^3 without

exhaust ventilation and 0.4-5.7 mg/m^3 with ventilation. Although this data is presented from an industrial hygiene standpoint, it indicates the generation capability of high intensity plasma arcs in industry.

4 HEATING TO EVAPORATION

Rather than imparting electric energy to the metallic material as quickly as possible in a violent action, such as the electric arc and exploding wire, other researchers have studied the effect of applying a steady source of heat: dirdctly, as with a lower level of electric current; or indirectly, as with a furnace chamber. This also results in the vaporization of a steady stream of metal vapor which condenses into a submicron aerosol. Some controlling parameters include temperature of the material, composition and dimensions of the material, and dilution-carrier gas flow rate. In addition to the development of practical test aerosol generators, the purpose of many of the following studies was to further investigate the underlying principles involved in the evaporation/condensation mechanisms.

Turkevich[51] stated his purpose as not only examining the nature of air contaminant fumes, but also, from an acadmeic standpoint, determining how unordered gaseous atoms condense to ordered ultrafine particles. In the region in which molecules aggregate in sufficient numbers to promote condensation, theoretical and experimental evidence seems to indicate that a limiting lower particle size exists, based on the fact that surface tension (varying directly with the square of the radius) tends to disrupt the particle while lattice energy (varying directly with the cube of the radius) tends to hold the particle together. Thus, the point of formation of a particle is complex, involving many parameters. For his purpose, Turkevich felt that the particles produced by an exploding wire were too irregularly shaped. He attributed this to the nature of the particle formation, which he considered to be basically disintegration. A process which agglomerates or condenses is considered more uniform for the study purposes. Particles from two aggregation processes, DC electric arc and electrically heated wire, were examined. The smoke from the electric arc suggested that the shape of the submicron particle was often characteristic of the chemical composition of the parent material,

especially as the particle size decreased. Turkevich attempted to study the stages in the evaporation/condensation process by passing current through a tungsten wire enclosed in a vacuum chamber bell jar, and collecting particles or promoting condensation on collection surfaces (collodion grids, later used directly in electron microscope analysis) positioned at different distances from the wire. With a high vacuum (10^6 mm Hg) in the chamber, the vapor appeared to migrate to each surface before condensing on it, giving a similar uniform deposit on each, regardless of distance. As the pressure in the chamber increased, however, he was able to detect three distinct areas where different processes predominated: evaporation, nucleation, and coagulation. Evaluations of particles were based on the average size and the PSD. From his observations he concluded that the final diameter of the particle is inversely proportional to the rate of nucleation, a phenomenon observed by others.

Spurny and various co-workers[52-57] investigated the generation of metals and metal compounds by sublimation and vaporization. Spurny prefers condensation over spraying as a means of aerosol generation, stating that the former results in a more monodisperse, controllable, and reproducible aerosol[58]. Two methods which Spurny uses in most of his research are: 1) heating metals in a furnace (usually preferred for low melting point metals); and 2) passing current through a wire. The major difference between these methods is the time necessary to achieve a stable aerosol. Furnaces can take hours, while heated wires achieve steady-state conditions in a matter of minutes. In general, condensation methods can produce aerosols within a size range from 0.001 to 1 μm. Dilution to a concentration of 10^4 particles/cm^3 is necessary to prevent coagulation of the aerosol.

Heicklen and Luria[58] presented a review of experimental results on kinetics of homogenous particle nucleation and growth. They acknowledge that metal oxide data in this area is limited. The authors indicate three means by which heterogeneous nucleation can form a homogeneous particle: 1) condensation on an ion; 2) condensation on a neutral nucleating particle; and 3) coprecipitation of two or more species. Homogeneous nucleation occurs when a critical supersaturation is reached or a gas

phase reaction occurs. Metal ions react with O_2 to give metal oxides. Some rate coefficient data is given for these reactions.

4.1 Metal Oxides

In studies conducted by Maiwald[59] and Polydorova[60], a 0.5 mm tungsten wire was vaporized by heating the metal to 850°C in an air flow. A problem inherent to this approach is the continual decrease in wire diameter which increases the current per unit length unless the voltage is regulated. Presence of an oxide layer appears to increase σ_g. The oxygen content of the carrier gas could be decreased to limit the formation of oxide but then the gas stream's usefulness for inhalation tests would be affected unless O_2 additions were made. Results from EM analysis indicate that particles range from 0.03 to 0.5 μm and are coagulated. An increase in temperature caused an increase in particle size due to the increased coagulation.

A similar study was also conducted by Polydorova[61] with platinum wire. At high wire surface temperatures (1330-1510°C), platinum oxide forms on the surface. Since the vapor pressure of the oxide is less than that of the pure metal, platinum oxide aerosols are generated. The higher vapor pressure at higher surface temperatures generates larger particles in higher concentrations. Keeping temperature constant, an increase in air flow dilutes the vapor and reduces the coagulation rate. Aerosols in concentrations of 10^5 - 10^6 particles/cm^3 with size ranging from 0.018 to 0.048 μm were generated in low air flows (3-6 l/min).

Fumes of Fe, Zn, and Cd oxides were generated by heating small amounts of the metals until vaporization occurred.[62] These simulated welding and brazing fumes were used to compare the sampling efficiencies of two industrial hygiene filter samplers. All samples had data showing that most particles were < 1 μm. The authors cite work by Jarnuszkiewicz indicating that the major portion of welding fume is < 0.5 μm.

4.2 Metal Halides

Metal aerosols, specifically Ag, have been widely used in the study of ice and rain nuceleation. Requirements for an aerosol for this application include being continuous, steady-state, and free of combustion products and oversized particles. Barchet and McKenzie[63] generated silver iodide aerosols by electroplating nichrome wires with Ag, exposing them to I vapor to form a AgI coating, and then heating the wire by passing current through it. Particle production is controlled by sublimation from the wire and recondensation in the quench air. A broad range of particle sizes was obtained, with 7% <0.1 μm and a geometric mean diameter of 0.01 μm. They estimated that approximately 50% of the small particles were lost by coagulation and diffusion by the time the sample reached the condensation nuclei counter.

Another AgI aerosol generation approach was taken by Poc and Rolleau[64] to attempt to eliminate all impurities from possibly influencing the ice nucleating mechanism. A two-step procedure was used: first, passing pure dry N_2 over a crucible of Ag heated to 950°C to generate a pure Ag aerosol; and second, exposing this aerosol to a steady flow of I vapor. Electron microscopy indicated an Ag aerosol with a concentration of 10^6 particles/cm^3 and size range from 20 to 130 Å with a median value of 50A. The AgI aerosol was similar but finer, consisting of single spheres 30 Å and less (to below the limit of resolution of the microscope). The aerosol requirements for these specific applications are quite limiting in terms of generating rates. The rate achieved in this example is less than 0.1 g/m^3.

Sublimation of AgI and AgCl and vaporization of a mixture of $AgNO_3$ and KI in a furnace yielded aerosols in the range of 0.05 - 0.3 μm, with a median size of approximately 0.15 μm. Spurny et al.[53] observed that the aerosol size and concentration increased with an increase in temperature. Au and Ag aerosols ranging from 0.02 to 0.2 μm and a Te aerosol of 0.1 - 0.3 μm (with a σ_g low enough to be considered monodisperse) were generated in a double furnace.[66] The purpose of the double furnace is to attempt to reduce the PSD range by resublimation and recondensation of the primary

particles formed in the first furnace. Spurny also introduced various materials to the double furnace as fine powders in a gas stream of dry air or helium.[55] An Fe_2O_3 aerosol with a size range from 0.002 to 0.02 μm was produced with a vaporizing temperature of 450-800°C, well below the melting point (1535°C). The range of generation rate capability of this method is not given but Spurny stated that these aerosols could be useful in experimental aerosol physics and chemistry studies, filtration studies, and biological research. As a variation of the heated wire method, Spurny et al.[56,57] heated a hollow tube of platinum by passing an electric current through it; dry air flowing through the center of the tube carried away the evaporated metal. They again observed that the particle size increased with increasing temperature, but decreased with increasing gas flow rates.

4.3 Metallic Aerosols in Argon

A heat-pulse cloud chamber was used by Buckle and Pointon[65] to study the condensation of metallic aerosols in argon. A highly supersaturated vapor is produced by passing a current through a coil to flash-heat the metal sample above background temperature. The vapor rapidly cools and condenses to form a suspension of droplets or solid particles. Zn and Pb aerosols were produced in this way, but difficulties were encountered with Ca and Cd. The authors feel that the formation of micron-size metallic aerosols is attributed to nucleation and growth under conditions of large temperature and concentration gradients near the supersaturator. In continued studies of Cd aerosol formation, Buckle and Pointon[66,67] observed that the particles were shaped like prisms and spheroids with a variety of surface features; e.g., dished areas and concentric rings and layers. This roughened platelike surface effect was thought to be caused by room temperature condensation of additional vapor onto the aerosol particles. They noted that the PSD was constant and log-normal with a geometric mean of approximately 2 μm, regardless of particle configuration.

5 COMBUSTION

Melting and vaporizing metallic materials can be achieved by means other than heating; e.g., combustion, feeding the material into a flame,

or combining it with combustible materials and igniting the mixture. Methods of generating metal aerosols by combustion are more varied than the previously discussed methods since there are many ways of introducing the metal material into the flame. These methods would still be classified as condensation, however, since the original phase, whether liquid or solids, if vaporized in the flame, then followed by condensation.

The problems of removing submicron-size iron fumes from open-hearth furnaces were studied by Billings et al.[68] in the mid-1950's using combustion to generate Fe_2O_3 for laboratory tests. Actually, two methods were used: 1) flake iron powder was injected into the air side of an air/oxygen/acetylene flame where it was oxidized exothermally; and 2) iron carbonyl was burned in an oxygen/acetylene flame. The second method provided a somewhat more controlled generation. Concentrations from these procedures ranged from 0.04 to 0.50 gr/ft^3. In field tests, they found furnace emission concentrations of 0.02-0.34 gr/ft^3. A particle size analysis of the furnace emissions indicated a mass median diameter of 0.65 - 0.82 μm, while the CMD was 0.047 - 0.057 μm. Thus even in earlier research with metal aerosols, the necessity for simulation of actual emissions was recognized.

Almost 20 years later another group of researchers, Brain et al.[69], modified the same equipment to continue the study of Fe_2O_3 aerosol generation from iron pentacarbonyl. They bubbled N_2 through the $Fe(CO)_5$ and decomposed the vapor in a 500°C furnace cylinder. A concentration of 340 mg/m^3 was achieved, composed of an agglomerated polydisperse aerosol with a CMD of 0.4 μm (σ_g = 2) and a mass median diameter of 1.6 μm. The primary spherical particles which make up the log-normal distributed agglomerates range in size from 0.01 - 0.03 μm. The authors estimated that the agglomeration occurs rapidly (with a half-time of 0.1 second) in the furnace. Keeping the furnace temperature above 500°C greatly reduces the toxic fumes and CO, making the aerosol suitable for animal studies.

A generator to produce uranium fume, U_3O_8, was devised by Glauberman and Breslin[70] in the mid-1950's. A bed of uranium chips supported on a slowly rotating wire mesh turntable was burned in an argon/oxygen gas

stream. The authors demonstrated that the median particle size could be pre-selected in a range of 0.05 - 0.2 μm (σ_g of 2.5-3.1) by establishing the appropriate argon to oxygen ratio and total gas flow rate. Their particular chamber design allowed sustained generation for 6 minutes.

Formenti et al.[71], working mainly with TiO_2, prepared metal oxide aerosols by carrying the vapor of metal chlorides into an oxygen/hydrogen flame. They observed both spherical and polyhedral (crystal) nonporous particles in the size range of 0.01 - 0.2 μm. The major parameters influencing size and shape include gas flow rate, chloride concentration, flame temperature, and residence time in the flame. Juillet et al.[72] continued the research with many other metal chloride solutions. Both groups noted that the aerosol exhibited photocatalytic properties in the presence of ultraviolet light, properties not found in large or porous particles.

Larger quantities of material can be generated by spraying a dilute metal or metal salt solution in an atomizer burner. Dharmarajan and West[73] used this method to generate metal oxide aerosols in the size range of 0.1 - 10 μm. Additional work is needed to characterize the particle size, to determine the controllability of the particle size distribution, and to eliminate the soot that accompanies the metal oxides.

A similar approach was taken by Carroz et al.[74] to demonstrate continuous high mass flow rate generation of fresh, fine, inorganic particulate aerosols, to simulate emissions from coal power plants, electric arc and basic oxygen furnaces, and Zn smelters. The fume generation apparatus consists of a solvent burner with a spray nozzle, pressurized tank, and ductwork. Inorganic metallic oxides are generated from the burning flammable solutions of metal nitrates and other salts. The hot gases and excess air reduce agglomeration. They have obtained particle loadings as high as 16.8 g/m^3 and concentrations of 10^9 particles/cm^3. Analyses with an electric mobility aerosol analyzer, optical counter, condensation nuclei counter, thermal precipitator, and electron microscope have indicated that the aerosol consists of hollow spheres (approximately 20 μm) and chain aggregates with mass median

diameters of approximately 1 μm. Methods were developed to vary SO_2 concentration and particle resistivity to better simulate power plant emissions over a wide range of operating conditions. The method is very flexible and can be used to generate aerosols of many different oxides and chlorides. Data from all methods is summarized in Table 4.

6 DISPERSION

Various approaches to aerosol generation can be classified as dispersion processes. The basic difference between dispersion and condensation categories is that the former involves mainly physical processes; the other is related more to chemical processes and phase changes. Dispersion encompasses the formation of two types of aerosols, solid particles and liquid droplets.

Dispersion of solid particles, by grinding or resuspension of pulverized material, results in a highly polydisperse aerosol, with doubtful reproducibility and control of size, shape, and concentration. Brain et al.[69] cite mid-1950's references of the use of a Wright Dust Feeder and a commercial blender to resuspend iron oxide and iron powder. Problems stem from the fact that the closely packed, sometimes charged particles tend to remain agglomerated and do not represent actual emissions.

6.1 Liquid Droplets--General

Generation of liquid droplets can consist of four basic types: 1) nebulization; 2) spraying; 3) rotation (spinning disks); and 4) vibration.[75] These methods can be used with many kinds of solutions including those with a dilute concentration of solids suspended in the liquid. The droplets also can be treated after formation such as by heating to evaporate liquid, leaving a solid residue, or by thermal decomposition to alter the chemical composition of the material. By combining the many alternatives of dispersion generation, numerous aerosol generation techniques have been devised. Examples of some of these typical applications which generate metal aerosols are presented in this review.

Table 4. SUMMARY OF PARTICLE SIZE DATA FOR GENERATORS USING COMBUSTION

Author	Data Type	Result, μm
Billings[68]	Mass median diameter	0.65 - 0.82
	Count " "	0.047 - 0.057
Brain[69]	Mass median diameter	1.6
	Count " "	0.4
Glauberman[70]	Median particle size	0.05 - 0.2
Formenti[71]	Range	0.01 - 0.2
Dharmarajan[73]	Range	0.1 - 10
Carroz[74]	Mass median diameter	1.3

A number of researchers[75-77] have tested spinning disk aerosol generators using an iron oxide solution. A fairly monodisperse aerosol is attainable but only for diameters larger than 1 μm. Albert et al.[75] were able to generate iron oxide particles in the range of 1-8 μm. Smaller, less monodisperse aerosols can be made by utilizing the satellite drops rather than the larger drops (this wastes 90% of the mass). The disadvantages are that the particles need heat to stabilize their structure and that the particles cannot be used directly for inhalation studies. Because the air stream contains solvent vapors, the aerosol must be collected and then redispersed, making this an awkward research tool.

Spertell and Lippman[76] also had difficulties, producing only 200 particles/cm^3 and being unable to maintain a stable test aerosol for long intervals. Even using an aerosol concentrator, they could not generate a usable aerosol less than 3 μm.

Caplan et al.,[77] like Albert et al., were able to generate a fairly monodisperse aerosol, but only in the size range of 2-6 μm.

6.2 Using Liquid Droplets--Nebulizers

A Lauterbach nebulizer driven by compressed air was used by Casarett and Epstein[19] to aerosolize a suspension of Fe_2O_3. PSD data determined with electron microscope analysis indicated a CMD = 0.068 μm and σ_g = 1.62. The authors concluded that Fe_2O_3 was an adequate material for use in inhalation studies although continued work is needed to fully characterize the aerosol, especially in the area of solubility.

Waite and Ramsden[78] describe an ultrasonic nebulizer which generates radioactive, stable, insoluble particles of Fe_2O_3. A solution prepared from ferric chloride and ferric nitrate results in hollow spheres of Fe_2O_3 when the solution is nebulized and dried. These hollow spheres have a CMD of 0.03 - 0.5 μm when the initial solution droplets are 3 μm. The authors note that an aerodynamic median diameter (AMD) rather than CMD should be used to describe the diameter of the iron oxide aerosol since the spheres are hollow rather than solid. To make this conversion, the density of the aerosol particles is needed; it will be less than the

bulk density of iron oxide or of a solid iron oxide particle. Their observations show a significant drop in density between 0.55 and 0.3 μm. This process is not only interesting, but also useful in situations where the amount of material needed is limited.

The work of Raabe et al.[79] appears more promising but still only allows a small amount of aerosol to be generated. Solutions of metals in the form of oxalates, citrates, and tartrates are nebulized into droplets and then thermally decomposed in a furnace at 1150°C. A spherical oxide aerosol results with no organic solvent contamination. A zirconium oxide aerosol was generated and found to have a size of approximately 3 μm. The authors state that the more monodisperse the droplet distribution system is, the more monodisperse will be the final particles.

This project was continued by Kotrappa and Wilkinson,[80] using the Lovelace nebulizer, which the authors classify as a high specific output nebulizer. They generated droplets from a colloidal iron hydroxide solution which was nebulized and dried to form iron oxide particles in the range of 0.3 to 3.5 μm, with a particle material density of 2.56 g/cm^3 (density was independent of particle size).

Aqueous solutions of metallic carbonates, acetates, and oxalates were generated with Lovelace and Collison nebulizers by Horstman et al.[81] and Friedman and Horstman.[82] Cd, Ni, and Mn solutions were used. The droplets were dried in a furnace with temperature of 600-1000°C to decompose them to an aerosol with a mass median diameter of 0.15 -0.6 μm and σ_g of 1.8-2.6.

As a research tool the approach of generating liquid drops and treating them thermally appears useful, but larger, more continuous aerosol production has not yet been shown to be feasible.

7 SUMMARY

Exposure to metal or metallic compound submicron aerosols is widespread, both to workers in an industrial setting and to the general population. In fact, the metals industries are second only to power

plants in total nationwide man-made emissions to the atmosphere. Research in areas of effects and control of metal aerosols requires sources of test aerosols. Submicron aerosols are needed for inhalation experiments (deposition and clearance of particles in the lungs), air pollution control equipment testing, filter testing, and sampling instrumentation development and calibration. To be useful, however, the aerosol must be reproducible, with a predictable characteristic particle size and range of diameter. Moreover, to simulate industrial emissions of metal aerosols, the appropriate range of diameters is from 0.25 to 5.5 μm.

There are many possible methods for the generation of laboratory test aerosols. These methods can be on a continuous or a batch basis, with high or low concentrations and generation rates, and with monodisperse or polydisperse size distributions. The method to be chosen and the resulting aerosol depend on the requirements of the specific research being conducted.

Metal aerosol generation can be thought of as being in two major divisions, condensation and dispersion. Condensation includes the formation of new particles from a vapor state which has been created by evaporation, sublimation, or combustion of some parent material. Dispersion includes any method involving a redistribution of the parent material into a smaller particle size. This could include grinding for solids or some droplet formation mechanism for liquids and solids in a liquid suspension. Treatment of the drops after formation by application of heat for evaporation or thermal decomposition is sometimes utilized to alter the droplet characteristics into a more useful aerosol. Condensation aerosols are usually < 1 μm, mainly existing as agglomerate chains (0.4-0.8 μm typical sizes) composed of charged primary spherical particles (0.001-0.01 μm). Dispersion aerosols are usually > 1 μm, but are more controllable and generally more monodisperse than those formed by condensation.

The exploding wire generator has been studied and used for many years. With carefully regulated operation, a useful reproducible metal aerosol can be produced, but only in small amounts (the mass of the

wire is the limiting factor) and on a batch basis. A high coagulation rate and polydisperse aerosol are due to the local high concentration in the plasma following an explosion. Immediate dilution partially alleviates this problem.

The low intensity electric arc generator includes easily accessible components, but offers a low metal to aerosol conversion efficiency. The process, consisting of vaporizing and melting the metal electrodes, is not a highly controllable system due to the arc flame instability. The product is normally a polydisperse agglomerated aerosol whose reproducibility is not yet totally proven. It does, however, come closest to simulating industrial emissions; from that standpoint and because of its ease of operation, it is a worthwhile system. Generation rates as high as 8 g/minute have been reported. The high intensity arc offers a much higher conversion efficiency and vaporization rate and operates with a more controllable stable flame. Its aerosols are still somewhat polydisperse due to coagulation. Electrode transpiration dilution helps reduce the tendency to coagulate. Some difficulty has been noted in feeding the powderized material to the electric arc. It has been suggested that it may be most useful to utilize this process in the basic configuration of an arc struck across an electrode and a metal-filled crucible. Generation rates as high as 40 g/minute have been reported with the high intensity arc.

Heating metallic material to evaporation by passing current through the material or by direct heating in a furnace provides very small quantities of aerosol. Most experiments using this process are theoretical, investigating basic principles of evaporation and condensation. Since low concentrations are produced, coagulation is not as great a problem. Some difficulties occur when heating wires, since the constantly decreasing diameter creates a non-steady state current.

Combustion processes such as spray solvent burning have high generation rate capabilities. The exhaust gas stream containing the aerosol may be hot and contain products of combustion such as CO, NO_x, and H_2O which may be used to simulate exhaust gases found in the industrial source

under investigation. Combustion processes provide particles in the 0.01 to 10 μm range which simulate closely the range found in industrial sources.

Direct production of solid particles from grinding or redispersion methods is generally not too successful from the standpoint of uniform size and shape. Liquid droplet formation methods such as spray nebulization, spinning disks, and ultrasonic nebulization have been very successful producing monodisperse aerosols. Generally, however, these aerosols are > 1 μm. Researchers have not yet developed this into a continuous, high concentration method.

In summary, the ability to generate a known reproducible source of aerosols, specifically metallic, for laboratory and research purposes is very important. A variety of significant work has been conducted in this field. Of the techniques studied only electric arcs and combustion have demonstrated the capability for continuous generation of large quantitities of metal aerosols which simulate the particle size of industrial sources.

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